THE EFFECT OF SURFACE CONDITIONS ON REFLECTION AND SCINTILLATION SPECTRA OF CdS CRYSTALS
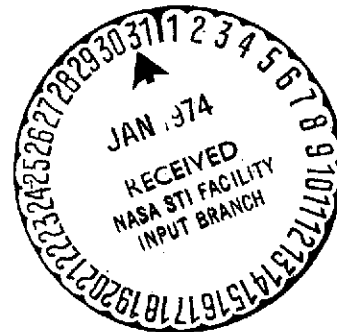
M. S. Brodin, A. V. Kritsky, E. N. Myasnikov,
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THE EFFECT OF SURFACE CONDITIONS ON REFLECTION AND SCINTILLATION SPECTRA OF CdS CRYSTALS

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In studying the nature of exciton spectra in semi-   *1824
conductive and other types of crystals, their reflection
spectra must often be measured. This is almost obli-
gatory for highly absorbing crystals where it is diffi-
cult to produce absorption spectra of single crystal
films which are fine enough for processing. As a rule,
this pertains to low temperatures, where the exciton
lines are narrow and there is an abrupt increase in their
maximum intensity. Clearly, measurement of reflection
spectra must be a function of surface conditions. There-
fore, in the frequency range near that of sharp intense
lines, the refractive index of surface layers may vary
with a slight shift in resonance frequency, which may
lead to interference phenomena in the reflected wave.

A detailed analysis of the form of low temperature
reflection spectra of CdS crystals of different qualities
was conducted. It was found that in using a neutral
etchant on spallation fragments or natural surfaces of
high quality crystals, the shape of the exciton line may
undergo cardinal changes. At the same time, a new scin-
tillation line is observed above the primary peak; this

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attests to the formation of a corresponding surface energy state. Appropriate experimental data will be given below, and the data will be discussed on the basis of theoretical interference phenomena due to the heterogeneity of the surface layer refractive index.

Experimental Findings

The reflection spectra of natural and etched edges of leaf and three-dimensional CdS crystals, as well as spallation fragments of bulk crystals, were measured at temperatures of 4.2 and 77° K. In this connection, single crystal specimens of very high quality were chosen. For three-dimensional single crystals, reflection spectra were measured for two directions of the wave vector K of incident light with respect to the optical axis of the crystal C: K $\perp$ C and K $||$ C. Moreover, the scintillation spectra were measured. All measurements were done with a spectrograph with an Abbe number of 4 Å/mm.

At T = 4.2° K, the following results were obtained. In the case of reflection from unetched crystal surfaces, the exciton lines A, B, and C appeared quite clearly. They are of a typical reflecting shape: the reflection maximum shifts to the long-wave side from the absorption maximum; the minimum, accordingly, shifts toward the short-wave side. For this reason, such a shape of curves R(ν) are observed during reflection both from leaf and from

three-dimensional single crystals, from their natural edges and from spallated surfaces. However, the reflection 1825 curve amplitude from the natural edges of three-dimensional crystals is, as a rule, less than from spallation fragments or leaf crystals, i.e., the exciton lines of reflection are somewhat broadened.

After treatment with a neutral etchant, it was found that crystal reflection curves may be divided into two groups according to observed effects. The first group contains specimens whose spectrum does not change after surface etching. The second group is comprised of crystals whose reflection spectrum changes more or less considerably. With a frequency change in the reflection spectrum,
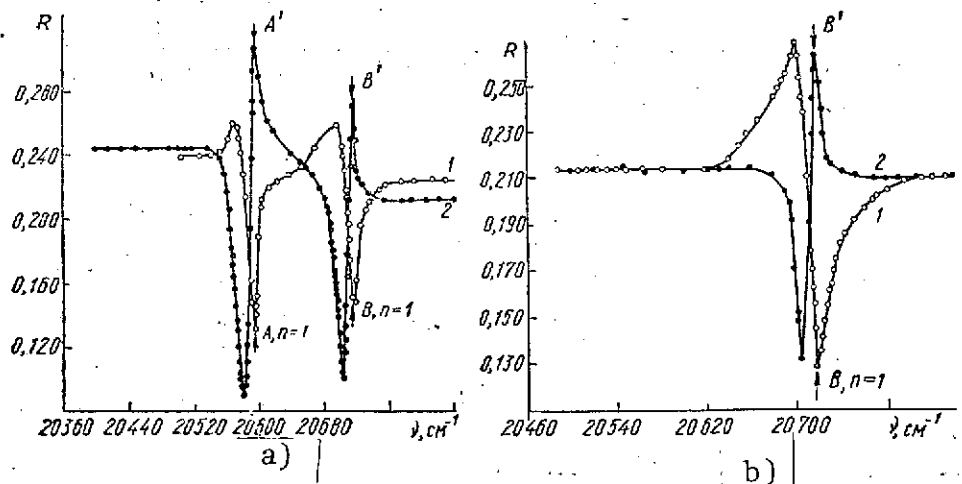

Fig. 1. Reflection spectra of CdS crystals at T = 4.2° K. a) $K||C$; $E \perp C$; b) $K \perp C$; $E||C$; 1) natural surface; 2) surface treated with etchant.

the maximum of curve R(ν) shifts toward the long wave end, and at the minimum, an additional reflection line, sharp and intense, appears. When the reflection curves change significantly, there is a virtually total "switch" in their shape: in place of the former reflection maximum the minimum is observed, and the maximum is observed instead of the former minimum. The latter case is illustrated in Figure 1a and b, where the change in the reflection spectrum after etching of the crystal surface is shown; in Fig. 2 the subsequent change in the appearance of the curves of R(ν) in proportion to an increase in the duration of etching is shown.

It should be noted that changes occur in the range of exciton lines A and B in both components of the spectrum ($E \perp C$ and $E||C$) and in two directions of the incident light wave vector ($K \perp C$ and $K||C$). In this connection, the considerably broadened line C (not shown in the figure) remains almost the same. The shifts of exciton line A noted in [1], where $K||C$ shifts toward the long wave side compared with the position where $K \perp C$, due to anisotropy of the effective mass of the exciton, is also observed in the altered reflection spectrum.

Changes in the reflection spectra occur identically during etching of both the surface of a natural crystal facet as well as of a surface spallation. Apparently,

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the most complete single crystal specimens with the smallest number of impurities, dislocations, and structural defects, belong in the second group, i.e., that of structures most closely approximating the ideal. Leaf and three-dimensional single crystals which have been grown by the "free growth" method and are in the form of six-sided prisms pertain to them.

Research on crystal luminescence drew considerable interest: the reflection spectrum undergoes significant changes at T = 4.2° K. Prior to etching the natural surface, a very feeble luminescence in the range of the free A exciton (which coincides in frequency with the maximum of the reflection curve) and doublets of bonded exciton states (so-called J_2 and J_5 lines) were observed. After etching, there was a significant increase in the intensity of all scintillation lines; the bonded exciton lines grew stronger, and their phonon iterations appeared. In the range of the free exciton, in addition to the previously observed emission line A ($\nu = 20,589$ cm^{-1}), additional luminosity A' ($\nu = 20,599$ cm^{-1}) appeared, which coincides in frequency with the new maximum of the reflection curve (Fig. 3). Both lines A and A' also have phonon iterations in the spectrum and are polarized with $E \perp C$.
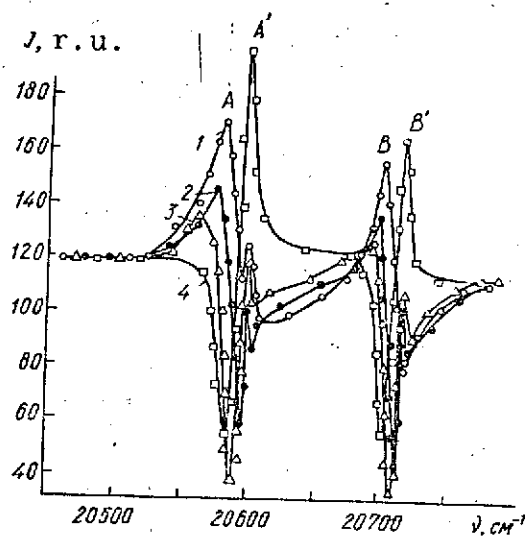
In the range of "green" luminescence both before and

Fig. 2. Shape of reflection spectrum of CdS crystal as a function of etching duration (T = 4.2° K, E⊥C, K⊥C); 1) etching time 1 min; 2) 3 min; 3) 4 min; 4) 5 min.

after etching, there was no luminescence observed, indicating the absence of centers responsible for such luminescence in the given specimen.

At temperatures up to 77° K, the described anomalies in the reflection spectra appear, and the shape of the curve R(ν) again becomes regular (Fig. 4). The luminescence line A' also appears.

Discussion of Findings

To a great extent, the indicated effects of etching in the reflection spectra can be explained if we consider that in crystals of the second group, as a result of etching, there is an increase or more evident manifestation of a surface potential barrier for excitons. Such

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a barrier may even exist in ideal crystals. This is shown in study [2] during examination of "surface transformation" forces acting on the exciton. In the same study, the potential barrier was, for simplicity's sake, replaced with a rectangle. Calculations showed that its existence leads to the formation of an additional maximum in reflection near frequency $\omega_{||}$ of long wave longitudinal excitons. However, it can be found that such a simplifying change does not allow stating in study [2] that the presence of a potential barrier can also lead to a substantial reduction in the reflection coefficient in the proximity of frequency ω_0 of transverse long wave excitons and to the formation of a reflection minimum in its place.

In reality, the presence of a potential barrier for excitons (as shown in study [3]) leads to a point where in the expression for dielectric permeance, the dispersion frequency ω_0 of a real crystal is a function of the distance x to the surface:

$$\varepsilon \approx \varepsilon_0 \frac{L_0}{\omega - \omega_0(x) + i\gamma} \qquad (1)$$

In analyzing the passage of electromagnetic waves through a medium with such dielectric permeance, two frequency ranges can be specified near $\omega_0(\infty)$, in which the role of the surface layer is quite distinct.
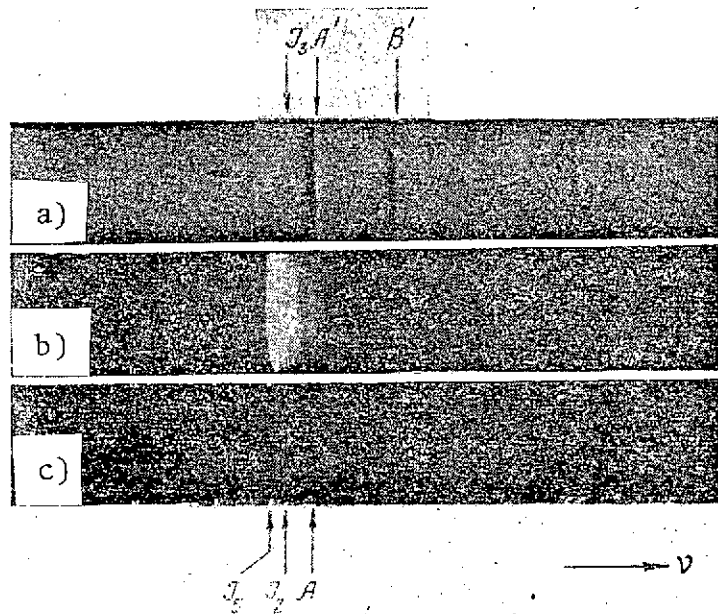
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Fig. 3. Comparison of reflection spectra (a) and scintillation spectra (b, c) in CdS crystals with natural surface at T = 4.2° K: a) etched crystal where $K \bot C$, $E \bot C$; b) etched single crystal CdS; c) non-etched surface. Scintillation spectra are produced at the same exposure where the weak line of the free exciton in the spectrum of the non-etched crystal did not appear.

If $\omega < \omega_0(\infty)$ and the crystal is almost transparent to waves of such frequency, then its optical boundary will be blurred by the width of the surface layer whose thickness increases in proportion to the proximity of ω to $\omega_0(\infty)$. When the transition layer is very thick, reflection will be slight. At small γ, when the width of the transition layer may be very great at frequencies ω close to $\omega_0(\infty)$, the reflection maximum decreases and will reach frequencies

$\omega < \omega_0(\infty)$.

In the other range $\omega > \omega_0(\infty)$, when the crystal is no longer totally transparent, the surface layer refractive index will be great. For this reason, its thickness will also be greater the closer ω is to $\omega(\infty)$. Interference of light in this layer can lead to the formation of one or even several interference extremes in this frequency range. If ω becomes greater than $\omega_0(\infty) + L_0/\varepsilon_0$, the effect of the surface layer abruptly decreases as the crystal becomes almost totally transparent. In this way, calculating the relationship $\omega_0(x)$ permits us, to a great extent, to explain the observation of reflection spectra features of the CdS crystal.

For instance, by the dispersion curves for formula (1), the parameters ε_0, L_0, γ and $\omega_0(\infty)$ can be evaluated as far as internal properties of the crystals appear in dispersion measurements. In Fig. 5, the dispersion curve is plotted, measured in a fine ($d \approx 0.3\mu$) "freely" bound leaf crystal of CdS at $T = 4.2°$ K. For the A exciton, $\varepsilon_0 \approx 8$, $L_0 \approx 100$ cm^{-1}, $\omega_0(\infty) \approx 20,585$ cm^{-1} and $\gamma \approx 2$ cm^{-1} were produced. In comparing the reflection spectra cal-   1828 culated from these data, characterizing the volumetric properties of the crystal, with the experimental data, we find that their divergence in the frequency range $\omega > \omega_0(\infty)$ can be explained by the effect of the transition layer.
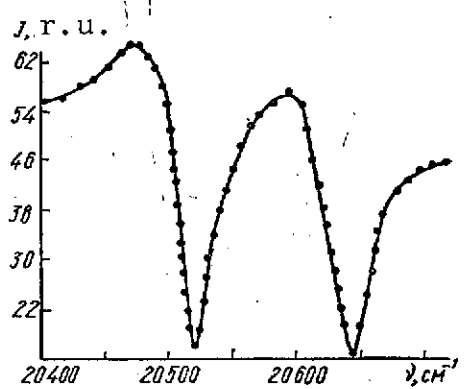
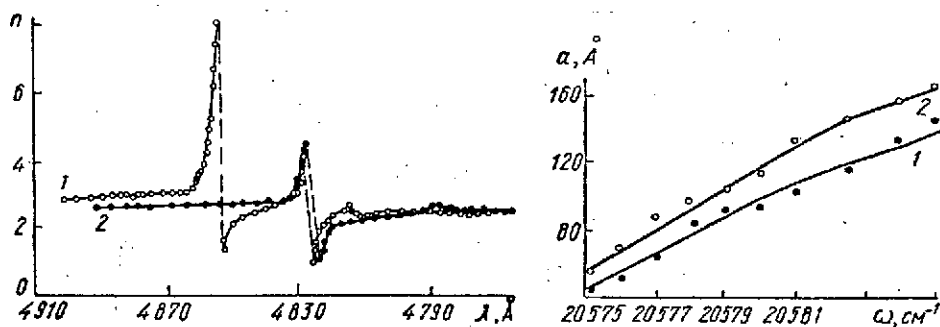Fig. 4. Reflection spectrum of CdS crystal, shown in Fig. la, curve 2, at T = 77° K.

Fig. 5. Dispersion curve of CdS crystal at T = 4.2° K: 1) $E \perp C$, 2) $E \| C$.

Fig. 6. Effective thickness of surface layer as a function of frequency: curve 1 calculated for curves of Fig. 5; in calculating curve 2, the reflection spectrum from the etched surface was used.

However, the effective thickness of this layer (a) must be a function of frequency as shown in Fig. 6 (curve 1). A similar calculation for an etched surface (curve 2 in Fig. 6) yields greater thickness of the transition layer

in the frequency range $\omega < \omega_0(\infty)$. The distance between
the graphs along the ordinate axis in Fig. 6 averages
20 Å. It can thus be concluded that on the crystal sur-
face as a result of etching a layer appears which has
variable properties and a thickness of this order.

A detailed investigation from this point of view of
the reflection spectrum in the range $\omega_0(\infty) < \omega < \omega_0(\infty)$
$+ L_0/\varepsilon_0$ allows us to state that only in crystals with in-
verted spectrum shapes two interference extremes can be
observed: a minimum with frequency of about $\omega_0(\infty)$ and a
maximum with frequency of about $\omega_0 + L_0/\varepsilon_0$. In all other
cases only the minimum is observed, and interference inten-
sifications of reflection become less noticeable since they
must occur at a frequency of $\omega > \omega_0(\infty) + L_0/\varepsilon_0$. Only the
very edge of this interference maximum appears either in
the form of a weak burst near frequency $\omega_0(\infty) + L_0/\varepsilon_0$, or
simply as a more abrupt increase (this follows from stan-
dard crystal optics) in the coefficient of reflection R
with increased ω in that frequency range. If this is
actually observed, the interference minimum should cor-
respond to the thickness of the transparent surface layer
on the order of 500 Å.

There is no doubt that, without specifying the effect
of interference in the surface layer, we cannot expect
that between reflection spectra and absorption spectra

a correspondence can be found on the basis of the Kramers-Kronig correlation. The need for careful use of this correlation was indicated in study [4].

The disappearance of properties in the reflection spectrum at higher temperatures, as established above, begins to make more sense. Naturally, an increase in temperature leads to an increase in γ, and when this quantity equals the height of the potential barrier in units of $\hbar$, its effect becomes barely noticeable. Even less noticeable will be the effect of the potential barrier in optical spectra of excitons with low oscillating power.

Concerning the scintillation spectrum, the following is noted. Since the new scintillation line A' coincides in frequency with the new reflection maximum, it can be attributed to the appearance of "surface" exciton states whose resonance frequency depends on "volumetric" excitons. However, this frequency is close to the frequency of the longitudinal exciton, observed in absorption spectra [5] and therefore, luminescence of the longitudinal exciton from the upper polarization branch [6] may appear in it. Nonetheless, we were able to connect line A' with the luminescence of "surface" excitons since it is observed in a direction perpendicular to the crystal surface and polarized perpendicular to the optical axis of

the crystal ($E \perp C$).

The question also arises of why different crystals behave differently with respect to etching. We can assume that this is due to their different degrees of homogeneity. With less perfect specimens, γ increases significantly (just as at higher temperatures). This leads to reduction of the surface barrier effect on the shape of curve $R(\nu)$. On the other hand, with more perfect crystals, the surface barrier properties manifestly appear in spectral properties.